

O5	0.6418 (10)	0.9600 (5)	0.2737 (2)	0.063 (2)
C6	0.7380 (11)	0.7380 (6)	0.2253 (3)	0.037 (2)
N6	0.7360 (10)	0.8397 (5)	0.1974 (2)	0.042 (2)
C21	0.7855 (11)	0.8507 (6)	0.1453 (2)	0.034 (2)
C22	0.6034 (10)	0.8676 (6)	0.1141 (2)	0.031 (2)
O221	0.5107 (8)	0.7472 (4)	0.1101 (2)	0.0382 (12)
C221	0.3451 (13)	0.7280 (6)	0.1347 (3)	0.041 (2)
O222	0.2721 (9)	0.8043 (5)	0.1597 (2)	0.063 (2)
C222	0.2668 (14)	0.6011 (6)	0.1243 (3)	0.056 (2)
C23	0.6530 (11)	0.9100 (6)	0.0620 (2)	0.028 (2)
O231	0.4745 (7)	0.9412 (4)	0.0380 (2)	0.0362 (12)
C231	0.4327 (12)	0.8847 (7)	-0.0049 (3)	0.039 (2)
O232	0.5260 (10)	0.8002 (5)	-0.0226 (2)	0.057 (2)
C232	0.2608 (13)	0.9428 (8)	-0.0282 (3)	0.051 (2)
C24	0.7753 (11)	1.0225 (6)	0.0643 (2)	0.035 (2)
O241	0.8220 (8)	1.0550 (4)	0.0138 (2)	0.0396 (13)
C241	0.8555 (13)	1.1788 (7)	0.0042 (3)	0.043 (2)
O242	0.8753 (11)	1.2541 (5)	0.0360 (2)	0.070 (2)
C242	0.8732 (14)	1.2017 (8)	-0.0494 (3)	0.057 (2)
C25	0.9526 (12)	0.9925 (7)	0.0937 (3)	0.046 (2)
O26	0.8952 (8)	0.9627 (5)	0.1434 (2)	0.0444 (14)

Table 2. Selected geometric parameters (Å, °)

N1—C2	1.338 (10)	C4—C5	1.456 (11)	
N1—C6	1.374 (9)	C5—N5	1.360 (10)	
C2—N3	1.325 (10)	C5—C6	1.422 (10)	
C2—S1	1.735 (8)	N5—O5	1.288 (9)	
S1—C12	1.722 (10)	C6—N6	1.319 (9)	
N3—C4	1.345 (10)	N6—C21	1.455 (9)	
C4—O4	1.222 (9)			
C2—N1—C6	114.3 (6)	N5—C5—C6	127.0 (7)	
N3—C2—N1	125.7 (7)	N5—C5—C4	115.2 (6)	
N3—C2—S1	113.4 (6)	C6—C5—C4	117.8 (7)	
N1—C2—S1	120.9 (6)	O5—N5—C5	116.2 (6)	
C12—S1—C2	103.4 (4)	N6—C6—N1	118.8 (6)	
C2—N3—C4	124.1 (7)	N6—C6—C5	117.9 (7)	
O4—C4—N3	120.7 (8)	N1—C6—C5	123.3 (6)	
O4—C4—C5	124.6 (8)	C6—N6—C21	128.0 (6)	
N3—C4—C5	114.7 (7)			
N1—C2—S1—C12	-12.8 (9)			
C6—C5—N5—O5	3.1 (13)			
C22—O221—C221—O222	-0.5 (10)			
C23—O231—C231—O232	7.4 (10)			
C24—O241—C241—O242	11.4 (13)			
D—H...A	D—H	H...A	D...A	D—H...A
N3—H3...O222 ¹	0.86	2.05	2.892 (8)	168
N6—H6...O5	0.86	1.81	2.516 (8)	138

Symmetry codes: (i) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$.

It was not possible to determine the absolute configuration of the title molecule from the X-ray data, but the absolute configuration of the β -D-xylopyranosyl moiety was known from the synthetic work and the coordinates were chosen to have this known configuration. Difference maps showed that the methyl H atoms at C12 and C242 were disordered. This was allowed for by placing six 0.5 occupancy H atoms in appropriate positions at each atom. The diagram (Fig. 1) was prepared using ORTEPII (Johnson, 1976) as implemented in PLATON (Spek, 1995a). Examination of the structure with PLATON showed that there were no solvent accessible voids in the crystal lattice.

Data collection: CAD-4/PC Software (Enraf-Nonius, 1992). Cell refinement: Enraf-Nonius SET4 (de Boer & Duisenberg, 1984) and CELDIM. Data reduction: DATRD2 NRCVAX94 (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: SOLVER NRCVAX. Program(s) used to refine structure: NRCVAX94; SHELXL93 (Sheldrick, 1993). Molecular graphics: NRCVAX94; PLATON; PLUTON (Spek 1995b). Software used to prepare material for publication: NRCVAX94; SHELXL93 and WordPerfect.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles, together with a view of (I) in the (100) projection, have been deposited with the IUCr (Reference: AB1309). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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5-Hexylamino-1,2-benzoquinone 2-Oxime Monohydrate

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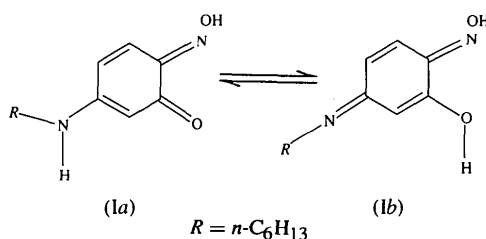
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Abstract

In C₁₂H₁₈N₂O₂.H₂O, the oximic OH group is *anti* (*trans*) to the quinoid carbonyl group, thus there are no intramolecular hydrogen bonds in the molecule. Extensive intermolecular interactions between neighbouring quinone oxime molecules and associated water molecules are observed. Bond distances are intermediate between those predicted for the 1,2-quinone oxime and 2,5-oxime imino forms.

Comment

Structural studies of 2-nitroso-substituted phenolic compounds have been widely reported (Fischer, Golding & Tennant, 1965; Hadzi, 1956; Norris & Sternell, 1966; Bartindale, Crowder & Morley, 1959). Such studies have shown that these compounds exist largely in the 1,2-quinone monooximic form (*Ia*) in the solid state and exhibit geometric isomerism centred on the orientation of the oximic OH group relative to the quinoid carbonyl group (Romers & Fischmann, 1960; Romers, 1964). Like the 5-hydroxy-substituted 1,2-benzoquinone monooximes (Charalambous, Christidis, Dodd, McPartlin, Pathirana & Talee, 1991), amino-substituted 1,2-quinone monooximes could exist in several other isomeric forms. To date, no structural studies on amino-substituted 1,2-quinone monooximes have been reported. Thus, in this paper, we report the structure of 5-hexylamino-1,2-benzoquinone 2-oxime monohydrate, (*I*), in order to demonstrate the effect of the inclusion of the amino group on the overall geometry of, and the electron-density distribution within, the 1,2-quinone monooximic moiety.



The bond distances C2—C3 [1.398 (5) Å] and C3—C4 [1.397 (4) Å] are the same, the C2—O2 bond [1.281 (4) Å] is longer than the average quinoid carbonyl C=O bond [1.222 (4) Å] (Boyens, 1976; Saarinen, Korvenranta & Naasakala 1977*a,b*) while the N7—C4 bond [1.330 (4) Å] is shorter than the average C_{sp^2} —NHR bond distance [1.339 (1)–1.416 (18) Å] (Bowen, Donohue, Jenkin, Kennard, Wheatley & Whiffen, 1958; Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). These bond lengths are intermediate between those that would be expected for forms (*Ia*) and (*Ib*). Satisfactory structure refinement was achieved with an H atom placed on N7 and none on O2, consistent with form (*Ia*), but H-atom location with X-ray data of this quality cannot be regarded as totally certain.

Compound (*I*) displays extensive intermolecular interactions between neighbouring quinone monooximic molecules and with associated water molecules. Thus, hydrogen bonds are found between the amino H atom and the quinoid carbonyl O atom on neighbouring molecules $\text{N7}\cdots\text{O2} = 2.930 (4) \text{ \AA}$ (O2 at $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$). In addition, strong hydrogen bonds are observed between the water O atom and the oximic H atom [$\text{O1}\cdots\text{O3} = 2.606 (4) \text{ \AA}$], and between the water H atoms and the quinoid carbonyl O atom [$\text{O3}\cdots\text{O2}(x - 1,$

$y, z) = 2.791 (4) \text{ \AA}$; $\text{O3}\cdots\text{O2}(x - \frac{1}{2}, \frac{1}{2} - y, 1 - z) = 2.820 (3) \text{ \AA}$].

The C8—C13 alkyl chain is affected by very high thermal motion. Thus, the bond distances and bond angles found here are less reliable than those of the carbocyclic ring. The alkyl chain does not present a normal zigzag conformation but two of the C—C bonds have a conformation approximating to *gauche* rather than staggered.

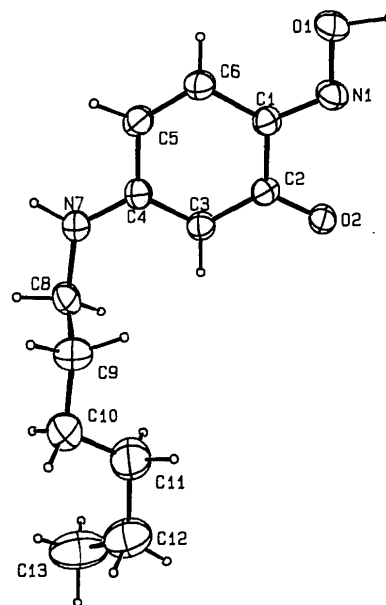


Fig. 1. The molecular structure of 5-hexylamino-1,2-benzoquinone 2-oxime showing the stereochemistry and relevant atomic numbering scheme. Displacement ellipsoids are plotted at the 30% probability level.

Experimental

5-Hexylamino-1,2-benzoquinone 2-oxime monohydrate was obtained by ion-exchange chromatography of the corresponding nickel(II) complex. The resultant orange solid recrystallized as octagonal crystals from a mixture of water and methanol (1:3).

Crystal data

$\text{C}_{12}\text{H}_{18}\text{N}_2\text{O}_2 \cdot \text{H}_2\text{O}$
 $M_r = 240.31$
 Orthorhombic
 $P2_12_12_1$
 $a = 8.016 (1) \text{ \AA}$
 $b = 11.552 (1) \text{ \AA}$
 $c = 14.409 (2) \text{ \AA}$
 $V = 1334.3 (3) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.196 \text{ Mg m}^{-3}$

Cu $K\alpha$ radiation
 $\lambda = 1.54184 \text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 40\text{--}48^\circ$
 $\mu = 0.67 \text{ mm}^{-1}$
 $T = 293 (2) \text{ K}$
 Prism
 $0.70 \times 0.35 \times 0.25 \text{ mm}$
 Orange

Data collection

CAD-4 diffractometer
 ω - 2θ scans

$R_{\text{int}} = 0.026$
 $\theta_{\text{max}} = 70^\circ$

Absorption correction: $h = 0 \rightarrow 9$
 empirical (North, Philips
 & Mathews, 1968) $k = 0 \rightarrow 14$
 $T_{\min} = 0.54$, $T_{\max} = 0.89$ $l = -17 \rightarrow 17$
 2853 measured reflections 3 standard reflections
 1487 independent reflections frequency: 120 min
 1198 observed reflections intensity decay: 2.3%,
 $[I > 3\sigma(I)]$ decay correction applied

Refinement

Refinement on F^2 $(\Delta/\sigma)_{\max} = 0.03$
 $R = 0.046$ $\Delta\rho_{\max} = 0.16 \text{ e } \text{\AA}^{-3}$
 $wR = 0.023$ $\Delta\rho_{\min} = -0.12 \text{ e } \text{\AA}^{-3}$
 $S = 1.12$ Extinction correction:
 1198 reflections Zachariasen (1963)
 234 parameters Extinction coefficient:
 H atoms positioned 8.728×10^{-7}
 experimentally, then all Atomic scattering factors
 H-atom parameters refined from *International Tables*
 $w = P/F_o$ if $F_o \geq P$; for *X-ray Crystallography*
 $F_o/2P < P$; $P =$ (1974, Vol. IV)
 $F_{o,\max}/3$

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$B_{\text{eq}} = (1/3) \sum_i \sum_j B_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	B_{eq}
O1	0.0250 (3)	0.4315 (2)	0.3845 (2)	5.31 (5)
O2	0.4983 (3)	0.3162 (2)	0.4012 (1)	4.13 (4)
O3	-0.1687 (4)	0.2634 (2)	0.4387 (2)	5.37 (5)
N1	0.1814 (4)	0.3877 (2)	0.3909 (2)	4.24 (5)
N7	0.6521 (4)	0.6188 (2)	0.1952 (2)	4.63 (6)
C1	0.2938 (4)	0.4537 (3)	0.3528 (2)	3.80 (6)
C2	0.4664 (4)	0.4084 (3)	0.3551 (2)	3.61 (5)
C3	0.5874 (5)	0.4655 (3)	0.3023 (2)	3.94 (6)
C4	0.5469 (5)	0.5650 (3)	0.2520 (2)	3.96 (6)
C5	0.3804 (5)	0.6145 (3)	0.2593 (2)	4.55 (7)
C6	0.2608 (5)	0.5625 (3)	0.3076 (2)	4.39 (6)
C8	0.8197 (5)	0.5774 (3)	0.1725 (2)	5.20 (7)
C9	0.8157 (7)	0.4900 (4)	0.0942 (3)	6.80 (1)
C10	0.9844 (8)	0.4393 (4)	0.0644 (3)	7.60 (1)
C11	1.0361 (9)	0.3411 (5)	0.1239 (3)	8.70 (1)
C12	1.1940 (1)	0.2751 (5)	0.0889 (3)	9.20 (1)
C13	1.3500 (1)	0.3476 (6)	0.0912 (4)	11.10 (2)
HO1	-0.047 (7)	0.361 (3)	0.408 (2)	3.8 (9)
HO3B	-0.16 (1)	0.227 (5)	0.503 (5)	7 (1)
HO3A	-0.290 (7)	0.283 (3)	0.432 (2)	3.7 (9)

Table 2. Selected geometric parameters (\AA , $^\circ$)

O1—N1	1.355 (4)	C3—C4	1.397 (4)
O2—C2	1.281 (4)	C4—C5	1.456 (5)
N1—C1	1.302 (4)	C5—C6	1.328 (5)
N7—C4	1.330 (4)	C8—C9	1.514 (6)
N7—C8	1.463 (5)	C9—C10	1.535 (8)
C1—C2	1.479 (5)	C10—C11	1.481 (7)
C1—C6	1.440 (5)	C11—C12	1.56 (1)
C2—C3	1.398 (5)	C12—C13	1.51 (1)
O1—N1—C1	113.1 (3)	N7—C4—C5	116.3 (3)
C4—N7—C8	124.6 (3)	N7—C8—C9	111.4 (3)
N1—C1—C2	115.5 (3)	C8—C9—C10	116.4 (4)
N1—C1—C6	125.1 (3)	C9—C10—C11	112.2 (4)
O2—C2—C1	119.4 (3)	C10—C11—C12	114.5 (5)
O2—C2—C3	122.4 (3)	C11—C12—C13	113.5 (5)
N7—C4—C3	123.8 (3)		
N7—C8—C9—C10	-179.6 (3)	C9—C10—C11—C12	172.1 (5)
C8—C9—C10—C11	83.6 (5)	C10—C11—C12—C13	65.6 (6)

Unit-cell parameters and intensity data were collected on an Enraf-Nonius CAD-4 diffractometer. All calculations were performed using SDP software (B. A. Frenz & Associates Inc., 1985) on a MICROVAX-3100 computer. Structure solution was carried out by direct methods using MULTAN80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980).

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: HA1110). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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